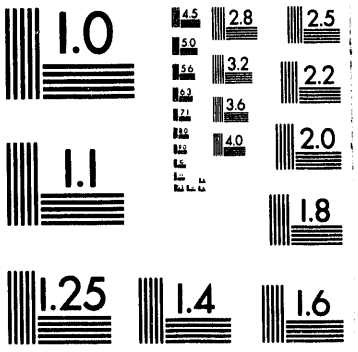
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DISSOCIATIVE RECOMBINATION OF H_3^+

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ABSTRACT

Recent experiments by Larsson et al.[1] have confirmed the prediction[2] of a high energy (~ 9.5 eV) peak in the cross section for dissociative recombination of H_3^+. This peak is caused by four doubly excited resonance states of H_3. Electron scattering calculations using the complex Kohn method provide resonance positions and widths as functions of the internuclear geometry. This information was used as input to a wave packet calculation for the dissociation dynamics on a fit to the resonant state potential energy surfaces. The resulting cross sections agree well with this experiment.

INTRODUCTION

A great deal of theoretical work exists on the dissociative recombination (DR) of diatomics.[3] In contrast there is little work on polyatomic systems. We have initiated a study on the resonant dissociative recombination of H_3^+[4,5]:

$$e^- + H_3^+ \rightarrow H_3^* \rightarrow H_2(v, J) + H$$
$$\rightarrow H + H + H$$

To our knowledge this is only *ab initio* treatment of DR that includes more than one nuclear degree of freedom. There has been considerable interest in the dissociative recombination of H_3^+ due to its importance in low-energy plasmas, particularly in the modeling of Jovian atmospheres and the interstellar media. In recent measurements of the DR cross section a high energy resonance peak was reported near 9.5 eV.[1] In earlier theoretical studies[2] a resonance in this energy range was found and predicted to contribute to the DR process. In resonant or 'direct' DR, the electron is captured into a resonance state of the neutral molecule. After capture, the molecule begins to dissociate. During this time, the molecule can autoionize, leaving the ion in a vibrationally or rotationally excited state. Once the resonance curve crosses the ionic curve and becomes bound with respect to the emission of an electron, autoionization can no longer occur, and the system evolves into asymptotic final states. Thus to describe the direct DR process one must know the energies and widths of the resonant states and describe the dynamics of the dissociative process. We will first describe how the potential surfaces and widths were determined, then how the dynamics was performed, and finally summarize our results.

CALCULATION OF RESONANCE POSITIONS AND WIDTHS

The ground state equilibrium geometry of H_3^+, an equilateral triangle[4], (D_{3h} symmetry) with bond lengths 1.65 a_0 is shown in Figure 1.

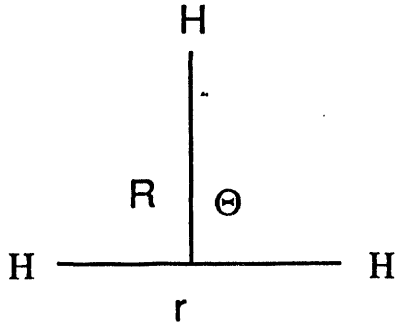

Figure 1: Coordinate system used in calculation. The equilibrium geometry is defined by $r_{eq} = 1.65a_0$, $R_{eq} = 1.4289a_0$, $\Theta = 90°$.

The electronic configuration is $1a_1'^2$. The resonance states correspond to the capture of an electron into the low-lying doubly degenerate e' orbital, with the simultaneous promotion of one of the a_1' electrons to the same orbital:

$$H_3^+ (1a_1'^2) + e^- \rightarrow H_3 (1a_1'1e'^2)$$

Because of the degeneracy of the doubly occupied orbital, four distinct molecular configurations are possible.

If we allow the molecule to distort keeping two of the bond distances equal, the D_{3h} symmetry is broken. In the resulting C_{2v} geometry there are four distinct states, two $^2A_1$ states:

$$c_1 1a_1 2a_1^2 + c_2 1a_1 1b_2^2$$

and two $^2B_2$ states:

$$c_3 1a_1 (2a_1 1b_2)^1 + c_4 1a_1 (2a_1 1b_2)^3$$

where the superscript in the last two cases represents the spin coupling of the two electrons in the parentheses. The coefficients, c_i, vary with nuclear geometry. We have found that all four states contribute to the observed peak in the DR cross section.

We carried out both restricted configuration-interaction (CI) calculations and electron-H_3^+ scattering calculations using the complex Kohn variational method[5] to map out the four resonance potential energy surfaces from the Franck-Condon region to the points where they cross into the bound state manifolds. These latter calculations are more complete because they correctly include the coupling of the resonance states

to the background and allow the determination of the resonance widths as well as positions.

The basis set used was the same as in our calculations[6] for dissociative excitation of H_3^+. At the equilibrium geometry of the ion (shown in Figure 1) six natural orbitals were selected, using the procedure outlined in Reference 6. At each new geometry, calculations on H_3 were carried out with these orbitals in the extended basis, with the restrictions that the $1a_1$ orbital remain singly occupied and not more than one electron is excited to the virtual space. This eliminates contributions from the background $1a_1^2\,ka_1$ and $1a_1^2\,kb_2$ states which represent a free electron in the field of the ion core. The results for these resonance states near the equilibrium geometry of H_3^+ are shown in Figure 2. The two $^2B_2$ states differ only by the spin-coupling of the two excited electrons, either singlet or triplet, and the curves are roughly parallel. By comparison there is a strong interaction between the two $^2A_1$ states with an avoided crossing exactly at the D_{3h} geometry. At these same points, the lowest $^2B_2$ and $^2A_1$ states become the degenerate components of the $^2E'$ state, leading to a *triple* intersection of electronic states along the symmetric stretch seam of the potential energy surface.

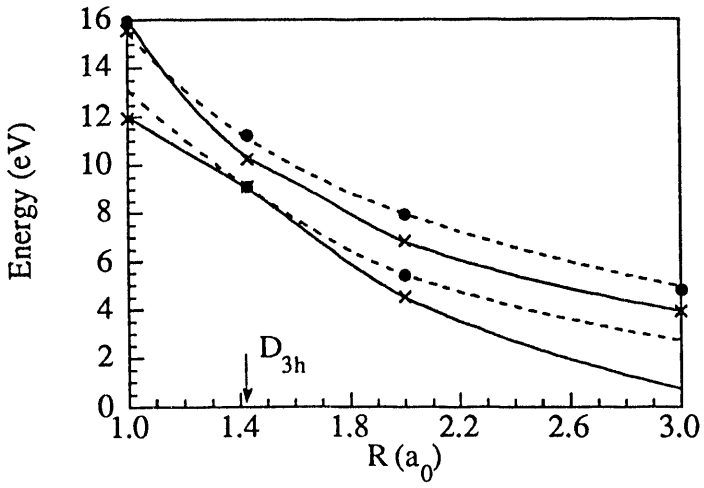

Figure 2: Cut through the H_3 potential energy surfaces. Θ is fixed at 90°, r is fixed at 1.65 a_0. The solid curves are for A_1 symmetry, the dotted curves are B_2 symmetry, derived from bound-state calculations. The symbols (X A_1, • B_2) are derived from electron scattering calculations.

In order to validate these bound state resonance calculations and obtain the resonance (autoionization) widths, electron scattering calculations from H_3^+ were carried out at a small number of geometries using the complex Kohn variation method.[5] The details of this method and its application to the dissociative excitation of H_3^+ have been described elsewhere.[6] The scattering calculation explicitly includes the effects of the continuum background. Carrying out scattering calculations at a series of energies, we can fit the eigenphase sums to a Breit-Wigner form to obtain the resonance widths and positions. For both symmetries we found it necessary to fit the

two resonances simultaneously. A typical example can be seen in Figure 3, where the eigenphase sum for elastic scattering of an electron from H_3^+ in A_1 symmetry for the molecule at its equilibrium geometry. The results for the potential energy surfaces of the resonance are shown in Figure 2. The two methods give the same shape for the surfaces with a shift of no more than ~ 0.5eV due to the coupling to the background.

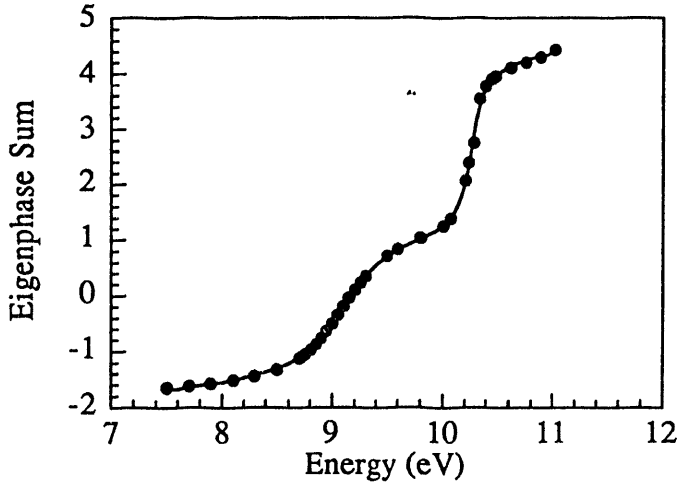

Figure 3: Eigenphase sums for electron - H_3^+ elastic scattering at the equilibrium geometry of the ion in A_1 symmetry. Solid circles are the calculated points, and the line is the fit to the sum of two Breit-Wigner resonance lineshapes.

In addition we carried out scattering calculations for Jacobi angle of 80°. The surfaces was found to be relatively flat near the C_{2v} geometries in this antisymmetric stretch degree of freedom. Therefore, the neglect of this degree of freedom should cause little change in the width or magnitude of the DR cross section.

DYNAMICS OF THE DISSOCIATION

Our calculation was carried out in C_{2v} geometries, thereby restricting the problem to two degrees of freedom. The dynamics was calculated using a wave packet method which involves the direct integration of the time dependent Schrödinger equation.

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi \qquad (1)$$

In Jacobi coordinates, shown in Figure 1, the initial wave function is defined on an r, R, grid, where r is the bond distance, and R is the distance from the remaining H to the center of mass of the H_2 bond. θ the angle between r and R was held fixed at 90°. In these coordinates, the Hamiltonian for the nuclear motion is given by,

$$H(r,R) = -\frac{1}{2\mu_1}\frac{\partial^2}{\partial r^2} - \frac{1}{2\mu_2}\frac{\partial^2}{\partial R^2} + V(r,R) \qquad (2)$$

where μ_1 is the reduced mass of H_2, μ_2 is the reduced mass of $H + H_2$. The potential energy is:

$$V(r,R) = V_0(r,R) + \frac{i\Gamma(r,R)}{2} \tag{3}$$

where V_0 is the real part of the resonance energy, and $\Gamma(r,R)$ is the complex portion (the resonance width). This is necessary since the resonant state can autoionize during dissociation.[7] The kinetic energies are evaluated by finite difference, and the time propagation was carried out using the Chebśyshev polynomial method.

Our treatment of dissociative recombination is a generalization of the time dependent treatment of photodissociation given by Kulander and Heller[8]. At t=0, the wave packet is defined to be

$$\Psi_0(r,R) = \sqrt{\frac{\Gamma(r,R)}{2\Pi}}\Phi_0(r,R) \tag{4}$$

$$= \sqrt{\frac{\Gamma(r,R)}{2\Pi}}\phi_i(Q_s)\phi_j(Q_b) \tag{5}$$

where $\phi_0(r,R)$ is the initial vibrational wave function on the resonant state surface, taken to be the simple product wave function of harmonic oscillator wavefunctions, $\phi_i(Q_s)$ and $\phi_j(Q_b)$ in the symmetric stretch and bending normal modes of H_3^+ for each initial vibrational state of interest.

From the time propagation of the wave packet on the dissociative surfaces, we can determine the total capture probability and the resonant dissociative recombination cross section. The total dissociative recombination cross section is calculated by projecting the final wave packet onto final states.[9] For example, when dissociation produces to an atom and a diatomic one can define:

$$S_2(E) = \sum S_i(E) \tag{7}$$

where the $S_i(E)$ are the final state probability distributions given by:

$$S_i(E) \propto \left| \iint drdR\chi_i(r)\phi_T(R)\Psi_t(r,R) \right|^2 \tag{8}$$

where $\chi_i(r)$ is a vibrational state eigenfunction of the diatomic, and $\phi_T(R)$ is the translation function describing the motion of the atom from the molecular center-of-mass, t is chosen large enough that the dissociation is complete, i.e.-the fragments are no longer interacting. This expression, when summed over all bound vibrational final states, yields the branching ratio into the two-body channel, $S_2(E)$. Once the sum in Eq.7 is extended to include the continuum H_2 states the result is the total dissociation cross section.

In Figure 4 we show the individual contributions of the four resonance states and the total DR cross section as a function of impact energy. These results are in quantitative agreement, both for the position of the peak and its shape and magnitude,

with the ~ 9.5 eV peak reported by high energy cross section measured by Larsson *etal.*[1]

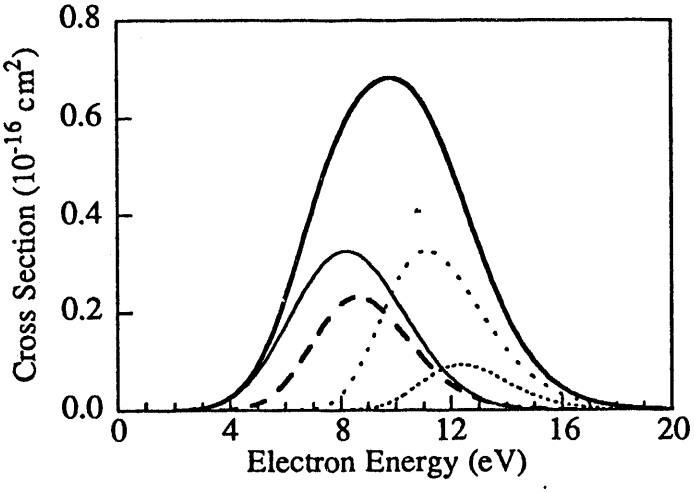

Figure 4: Total (heavy solid line) and partial resonance DR cross sections as a function of incident electron energy: 1^2A_1 (solid line), 1^2B_2 (long dashed line), 2^2A_1 (medium dashed line) and 2^2B_1 (short dashed line).

ACKNOWLEDGEMENTS

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